

PATENT SPECIFICATION

894,862

NO DRAWINGS.



Date of Application and filing Complete Specification :
Oct. 16, 1959. No. 35045/59.

Application made in United States of America on Oct. 20, 1958.

Complete Specification Published : April 26, 1962.

Index at Acceptance:—Class 2(6), P13D(2B:2C:2X:5A), P13F3, P13(T1X:TX).

International Classification:—C08f.

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ERRATA

SPECIFICATION NO. 894,862

Page 1, line 21, for "transistion" read "transition"

Page 3, line 99, for "E" read "R"

Page 4, line 8, for "100" read "1000"

THE PATENT OFFICE,
29th June, 1962

DS 65255/1(18)/R.109'200 6/62 PL

15 lar weight polymer fractions from high molecular weight polymer fractions.

20 Recently it was discovered that substituted olefins can be polymerized to high molecular weight polymers, i.e., polymers suitable for use as a plastic, by employing a catalyst obtained on reacting a transition metal compound and particularly halides of titanium, zirconium, vanadium, tungsten, molybdenum and chromium with a metal alkyl, Grignard reagent or metal hydride. It is believed that the metal alkyl and similar compounds react with the transition metal compound forming a complex containing the transition metal in a reduced valence state. The reduced transition metal is believed to co-ordinate with ethylenically unsaturated monomers and thereby cause their polymerization. These catalysts have therefore been referred to as co-ordination catalysts.

35 In the polymerization of substituted olefins to high molecular weight polymers employing these co-ordination catalysts, the polymers obtained, although of very high average molecular weight, contain a low molecular weight fraction due to the wide molecular weight distribution of the polymer. Although the molecular weight dis-

the present invention are high molecular weight polyolefins obtained through the homo-polymerization of an olefin having the general formula $R-CH=CH_2$ or $-R^1-CH=CH-$, where R is a monovalent

hydrocarbon radical which may be aromatic or aliphatic in nature and R^1 is a divalent aliphatic or cycloaliphatic hydrocarbon radical with a co-ordination catalyst which is preferably the reaction product obtained by admixing a transition metal halide selected from Group IV-B, V-B and VI-B of the Periodic Table (page 392 of 37th Edition of Handbook of Physics and Chemistry—Chemical Rubber Publishing Co.) with an organo-metallic compound having at least one metal to hydrocarbon bond. The polyolefins are generally crystalline polymers which have X-ray crystallinities of above 30% and which are generally characterized by solubility in hydrocarbon solvents at elevated temperature.

The low molecular weight fraction defined herein as grease is that polymer fraction which is soluble in hydrocarbon solvents at temperatures below the melting point of the polyolefin. Although low molecular weight polymer can be separated by extraction with

[Price 4s. 6d.]

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COMPLETE SPECIFICATION.

Separation of Polyolefins.

We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of
 5 Wilmington, State of Delaware, United States of America (assignee of Edwin David Johnson), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The process of the present invention relates to the separation of alpha-olefin polymers and in particular to the separation of low molecular weight polymer fractions from high molecular weight polymer fractions.

Recently it was discovered that substituted olefins can be polymerized to high molecular weight polymers, i.e., polymers
 20 suitable for use as a plastic, by employing a catalyst obtained on reacting a transition metal compound and particularly halides of titanium, zirconium, vanadium, tungsten, molybdenum and chromium with a metal
 25 alkyl, Grignard reagent or metal hydride. It is believed that the metal alkyl and similar compounds react with the transition metal compound forming a complex containing the transition metal in a reduced valence
 30 state. The reduced transition metal is believed to co-ordinate with ethylenically unsaturated monomers and thereby cause their polymerization. These catalysts have therefore been referred to as co-ordination
 35 catalysts.

In the polymerization of substituted olefins to high molecular weight polymers employing these co-ordination catalysts, the polymers obtained, although of very high
 40 average molecular weight, contain a low molecular weight fraction due to the wide molecular weight distribution of the polymer. Although the molecular weight dis-

tribution can be controlled to a certain degree by polymerization conditions, sufficient of the low molecular weight fraction remains in the polymer to significantly affect the properties of the polymer. The removal of this low molecular weight fraction, hereinafter referred to as grease, to the extent that it affects the polymer properties is highly desirable, since the grease tends to plasticize the polymer, thus decreasing such important properties of the polyolefins as its high temperature stability, stiffness, tensile strength and solvent resistance.

The polyolefins employed in the process of the present invention are high molecular weight polyolefins obtained through the homo-polymerization of an olefin having the general formula $R-CH=CH_2$ or $-R^1-CH=CH-$, where R is a monovalent

hydrocarbon radical which may be aromatic or aliphatic in nature and R^1 is a divalent aliphatic or cycloaliphatic hydrocarbon radical with a co-ordination catalyst which is preferably the reaction product obtained by admixing a transition metal halide selected from Group IV-B, V-B and VI-B of the Periodic Table (page 392 of 37th Edition of Handbook of Physics and Chemistry—Chemical Rubber Publishing Co.) with an organo-metallic compound having at least one metal to hydrocarbon bond. The polyolefins are generally crystalline polymers which have X-ray crystallinities of above 30% and which are generally characterized by solubility in hydrocarbon solvents at elevated temperature.

The low molecular weight fraction defined herein as grease is that polymer fraction which is soluble in hydrocarbon solvents at temperatures below the melting point of the polyolefin. Although low molecular weight polymer can be separated by extraction with

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hydrocarbon solvents, such a process is practical only for small polymer quantities. On a large scale, such an operation is time consuming and expensive, and furthermore does not give rise to a uniform product.

It has now been found possible to separate the grease, i.e. low molecular weight polymers, from the high molecular weight polymers by a process which can be carried out rapidly and continuously.

According to the present invention there is provided a process for separating high molecular weight crystalline polymer of an olefine having the general formula $R-CH=CH_2$ or $-R^1-CH=CH-$ wherein R is a monovalent aliphatic, cycloaliphatic or aromatic hydrocarbon radical and R^1 is a divalent aliphatic or cycloaliphatic hydrocarbon radical from low molecular weight polymer fractions thereof which comprises dissolving a mixture thereof in a solvent, heating the resulting solution to a temperature above the melting point of the polymer under sufficient pressure to maintain the density of the solvent vapour or liquid solvent in the polymer solvent phase above the precipitation density of the solvent, reducing the pressure to cause the density of the solvent in the vapour or polymer-solvent liquid phase to drop to below precipitation density and removing as separate streams, molten high molecular weight polymer and a solvent-low molecular weight polymer phase.

It is preferred to heat the solution to above the critical temperature of the solvent. Whilst the pressure is being reduced to cause the density of the solvent in the vapour or liquid polymer-solvent phase to drop to below the precipitation density it is preferred to maintain the temperature above the critical temperature.

By the use of the process of the present invention it has been found that difference in the density of a solvent vapour occurring under specific pressure and temperature conditions can be employed to separate high molecular weight linear polymers of ethylene from low molecular weight, polymer greases. Thus it was found that although the solubility of the solid polyolefin in hydrocarbon solvents generally increases with temperature, precipitation of the high molecular weight polymer occurs when a specific density of the solvent is reached by increasing the temperature. This density is referred to hereinafter as the precipitation density. It is characteristic of the solvent, and does not vary as between liquid and vapor phases. Thus, for example, crystalline polypropylene is practically insoluble in *n*-pentane at room temperatures but does go into solution at elevated temperatures, i.e. temperatures above 100° C. The polymer remains in solution over the range of 120°—180° C. but as the temperature reaches 180° C. the polymer

precipitates out of solution because the density is not sufficiently high enough to maintain the polymer in solution. If the temperature is then further increased above the critical temperature to about 210° C. and the pressure increased to approximately 1800 p.s.i., the polymer is redissolved in the super-critical vapor and can be precipitated again by decreasing the pressure to cause the density of the solvent in the polymer phase to drop below the precipitation density of the solvent.

The process of the present invention is preferably carried out at temperatures above the critical temperature of the solvent. Although the solvent can not exist as a true liquid at temperatures above the critical temperature, it is possible by increasing the pressure to increase the density of the solvent in the supercritical phase to above the precipitation density of the solvent and thus obtain a homogeneous polymer-solvent phase. If the density of the polymer-solvent phase is then decreased below the precipitation density of the solvent, by decrease in pressure, precipitation of the high molecular weight polymer will occur, which can then be removed as a separate phase. At temperatures above the critical temperatures only two phases exist, one the supercritical vapor phase containing the grease, and two the liquid polymer phase. Separation of the vapor from the liquid phase is readily accomplished due to the difference in gravity of the two phases. At temperatures above the critical temperature the density of the solvent is, furthermore, more readily controlled than at temperatures below the critical temperature, the control being accomplished by mere changes in pressure.

The process may be similarly employed at temperatures below the critical temperature of the solvent. In that case the density of the solvent in the polymer-solvent phase is controlled by the temperature and the fractions that are formed are a liquid high molecular weight polyolefin fraction and a low molecular weight polyolefin-liquid solvent fraction.

The exact temperatures and pressures under which the polymer separation of the present invention is effected vary with the solvent employed and the solid polyolefin and are dependent on the precipitation density and the critical temperature of the solvent. Critical temperatures of solvents may be obtained from such sources as International Critical Tables; Chemical Engineers Handbook by Perry; Data Book on Hydrocarbons by Maxwell. The precipitation density of the solvent for a particular polyolefin is readily determined by small scale experiments such as heating sample solutions of the polymer under known temperature and pressure conditions until the polymer precipitates out

of the polymer-solvent phase and calculating the density of the solvent from the pressure, the temperature, the volume of the solvent and known thermodynamic constants. In the table below are given the precipitation

densities of some of the polyolefin solvents with polypropylene. These values were determined employing samples of polymer solutions under autogeneous pressure

Polymer	Solvent	Critical Temperature in ° C.	Precipitation Temperature in ° C.	Precipitation Density in g/cm. ³
Polypropylene	pentane	197.2	180	0.39
..	n-hexane	234.8	215	0.39

The solvents employed in the process of the present invention are preferably hydrocarbon solvents, which are useful in the polymerization of the substituted olefin as polymerization media. Particularly suitable solvents are saturated aliphatic, cycloaliphatic and aromatic hydrocarbons having from 5 to 10 carbon atoms, such as the solvents listed hereinabove. The term "solvent" as employed in the present invention, also includes mixtures of one or more hydrocarbons of the class disclosed and mixtures of such hydrocarbons with lower boiling saturated hydrocarbons. The concentration of the polymer in the solvent does not affect the separation of the two phases; however, a more efficient separation of polymer and grease is obtained when the concentration of the polymer is less than 20% by weight of the solvent.

The process of the present invention is preferably carried out by dissolving the polymer in the solvent at elevated temperature, or employing a polymer solution obtained directly from the polymerization vessel after the catalyst residues have been removed, passing the resulting solution into a heat exchanger where the solution is heated, under sufficient pressure to maintain a homogeneous mixture, to a temperature above the critical temperature of the solvent and then passing the resulting supercritical vapor through a pressure letdown valve into an intermediate pressure separator. The intermediate pressure separator is maintained at a temperature above the critical temperature and at a pressure which results in a solvent density below the precipitation density. From the intermediate pressure separator the molten polymer and some residual solvent is taken off the bottom and solvent vapor and grease is taken off the top. The polymer can then be passed into a low pressure separator where the residual solvent is flashed off. The supercritical solvent vapor containing the grease is cooled to temperatures at which the solvent is liquid. The grease-solvent solution can be separated by distillation of the solvent. The distilled solvent can then be recycled to the

polymerization unit. The degree of separation of polymer from grease according to the process of the present invention will depend on how far below the precipitation density the density of the supercritical vapor is decreased in the separation step. The greater the difference between the precipitation density and the density maintained in the separation step, the less efficient is the separation of polymer and grease. The solvent density maintained during separation can, of course, be lowered to such a degree that the grease will precipitate with the polymer. Such lowering must, of course, be avoided in order for separation to occur. The density of supercritical vapor in the separation step will depend on the type of product desired. If it is desired to have a product containing little or no grease, the density of the vapor in the separator is just slightly below the precipitation density of the solvent. For some products small amounts of grease, less than 2% for instance, may be tolerated, since such quantities do not affect the properties significantly, but do facilitate fabrication. In such a case the density in the separation may be a little lower. Since the density of the solvent in the supercritical phase is accurately and easily controlled by pressure, the process of the present invention presents a highly versatile method for the separation of low molecular weight polymer fractions from high molecular weight polymer.

The process of the present invention is applicable to homopolymers of substituted olefins having the general formula $E-CH=CH_2$ and $-R^1-CH=CH-$, where R is an

aromatic, aliphatic or cycloaliphatic monovalent hydrocarbon radical, and wherein R^1 is a divalent aliphatic or cycloaliphatic hydrocarbon radical. Examples of the solid polyolefins in which the low molecular weight polymer fraction is removed by the described process include in addition to the ones shown in the examples polybutene-1, polystyrene, poly(3-phenylpropene-1), poly(3-phenyl-

butene-1), poly(4-phenylbutene-1), polyisobutylethylene, polyisopropylethylene, polybicyclo(2.2.1)-heptene-2, and polydihydrocyclopentadiene.

5 The process of the present invention is further illustrated by the following examples :

EXAMPLE I.

Into a 100 ml. autoclave was charged 30 g. of polypropylene as indicated below and 600

10 ml. of *n*-pentane. The mixture was heated with agitation under autogeneous pressure to form a polymer solution. The solution was then brought to the temperature and pressure conditions indicated in the table by further heating and/or injection of additional solvent. 15 A sample of the mixture was taken from the top of the autoclave and was found to have the composition indicated in the table.

20	Polypropylene Composition			Temp. ° C.	Pressure p.s.i.	Density g/cn. ³	Wt. of Grease in Sample	Wt. of Polymer in Sample
	100% low ml. wt.	210	500	0.12	0	—
	100% low ml. wt.	210	600	0.22	0.5 g.	—
	100% low ml. wt.	210	700	0.31	0.5 g.	—
25	100% high ml. wt.	214	800	0.33	—	0
	100% high ml. wt.	208	950	0.38	—	0
	100% high ml. wt.	209	1200	0.41	—	2 g.
	100% high ml. wt.	210	2150	0.45	—	3 g.
30	{ 25% low ml. wt.	209	850	0.36	2 g.	0
	{ 75% high ml. wt.					
	" " " "	208	1300	0.42	2 g.	2 g.

35 The table shows the separation of high and low molecular weight polypropylene as accomplished by change in pressure and also shows the three solubility stages of the supercritical vapor, i.e., both polymer and grease being dissolved, the polymer being insoluble and both polymer and grease being insoluble.

40 As can be seen from these results, the closer the precipitation density of the solvent in the solvent-polymer mixture is approached by control of temperature and pressure, the more complete is the separation of the polymer from the grease.

45 The above example has illustrated the process of the present invention with respect to *n*-pentane as solvent for the polymers. Although cyclohexane, because of its solubility characteristics is the preferred solvent, 50 the separation process is equally well applicable to other hydrocarbon solvents useful for dissolving high molecular weight solid polyolefins. The separation process may be employed on a continuous basis or batchwise. 55 The process of the present invention is particularly useful in combination with a polymerization process wherein the polymer is formed as a solution in the polymerization medium since such a process will eliminate 60 the need for a separate solution step.

WHAT WE CLAIM IS :—

1. A process for separating high molecular weight crystalline polymer of an olefine having the general formula $R-CH=CH_2$ or $R^1-CH=CH_2$ wherein R is a mono- 65

valent aliphatic, cycloaliphatic or aromatic hydrocarbon radical and R^1 is a divalent aliphatic or cycloaliphatic hydrocarbon radical from low molecular weight polymer fractions thereof which comprises dissolving a mixture thereof in a solvent, heating the resulting solution to a temperature above the melting point of the polymer under sufficient pressure to maintain the density of the solvent vapour or liquid solvent in the polymer solvent phase above the precipitation density of the solvent, reducing the pressure to cause the density of the solvent in the vapour or polymer-solvent liquid phase to drop to below precipitation density and removing as separate streams, molten high molecular weight polymer and a solvent-low molecular weight polymer phase. 70 75 80

2. A process as claimed in Claim 1 in which the polymer is polypropylene. 85

3. A process as claimed in Claim 1 or 2 in which the solution of polymers is heated to above the critical temperature of the solvent.

4. A process as claimed in any of Claims 1 to 3 in which the temperature is maintained above the critical temperature of the solvent whilst the pressure is reduced to cause the density of the solvent in the vapour or liquid polymer-solvent phase to drop below the precipitation density.
5. A process as claimed in any of Claims 1 to 4 in which the solvent is a hydrocarbon solvent.
6. A process as claimed in Claim 5 in which the solvent is a saturated aliphatic, cycloaliphatic or aromatic hydrocarbon having from 5 to 10 carbon atoms.
7. A process as claimed in Claim 6 in which the solvent is cyclohexane.
8. A process as claimed in any of Claims 1 to 7 in which the concentration of the polymer in the solution is less than 20% by weight of the solvent.
9. A process for separating high molecular weight crystalline polymer of an olefine having the general formula as defined in Claim 1 from low molecular weight polymer fractions thereof substantially as hereinbefore described with particular reference to and as illustrated in the foregoing example.
10. High molecular weight crystalline polymers of olefines having the general formula as defined in Claim 1 whenever obtained by a process as herein described and claimed.
- W. P. THOMPSON & CO.,
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Chartered Patent Agents.

Abingdon : Printed for Her Majesty's Stationery Office, by Burgess & Son (Abingdon), Ltd.—1962.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2,
from which copies may be obtained.